

Future Nanocharacterization with Electrons: sub-Ångstrom, sub-eV, and Single Atom

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Recent major advances in instrumentation are opening new avenues of investigation in materials transmission electron microscopy (TEM). For decades, image resolution in TEM and scanning TEM (STEM) has been limited by the 3rd order spherical aberration of the objective lens. In the last eight years, multipole aberration correctors have been developed,^{1, 2} and the first results are starting to appear from instruments with sub-Ångstrom spatial resolution.^{3, 4} Energy resolution in electron energy loss spectroscopy (EELS) has been limited by the energy spread of the electron source. Now high energy electron monochromators are enabling spectroscopy with <0.2 eV energy resolution.^{5, 6}

The capabilities of current or near-future TEMs and STEMs include: (1) imaging and chemical analysis of impurities with single atom sensitivity; (2) imaging and spectroscopy of point defects; (3) local valence-band spectroscopy; (4) 3D, nanometer-resolution imaging, and (5) coherent scattering at 0.5–5 nm length scales which is revealing structural order in materials that appear fully amorphous by other techniques.

The capability to image single atoms inside a crystalline material was first demonstrated using high-angle annular dark field “Z-contrast” STEM on Sb dopants in Si.⁷ Figure 1 is a Z-contrast image of Sb-doped Si grown epitaxially on an undoped substrate. The atomic columns in the substrate on the right are all the same intensity; some of the atomic columns in the doped material on the left are brighter, indicating they contain at least one Sb atom through the sample thickness. Statistical analysis of the bright column intensities of similar images reveals that ~85% of them contain only one Sb, proving single-atom sensitivity. Since that initial report, single La impurity atoms in CaTiO₃ have been detected by EELS.⁸ This points to the tremendously exciting possibility of measuring the local electronic environment around single impurity atoms. Monochromated EELS has also proved able to measure valence to conduction band transitions with nanometer spatial resolution, opening the possibility of measuring the band structure of individual nanostructures like quantum dots.⁹

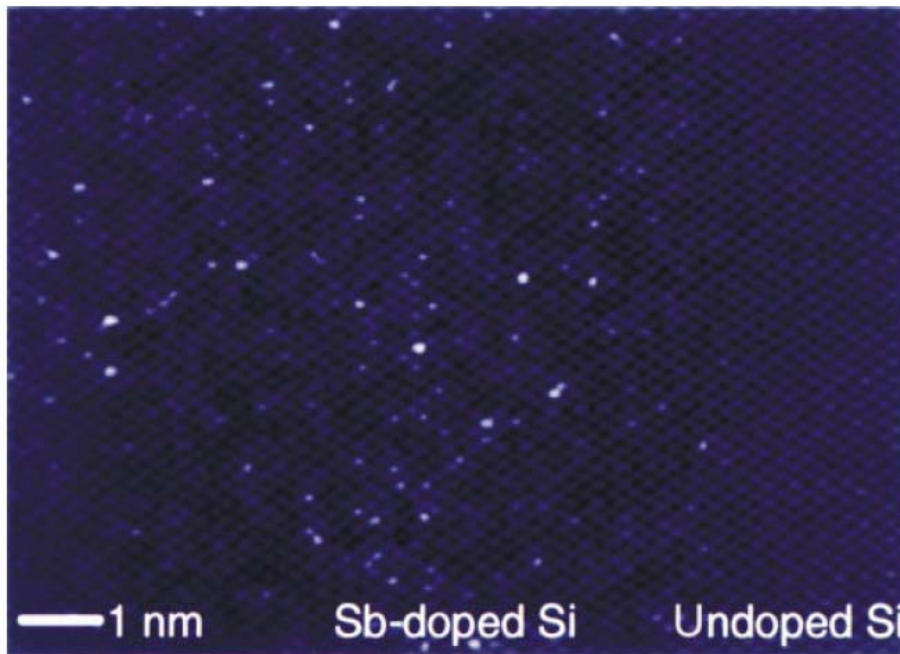


Figure 1: Z-contrast STEM image of Sb-doped Si grown epitaxially on an undoped substrate. Most of the brighter atomic columns in the

Imaging and spectroscopy in the STEM have also recently demonstrated the capability to characterize point defects. In SrTiO₃, a combination of spatially resolved EELS at the Ti L- and O K-edges EELS and strain-contrast low-angle annular dark-field imaging results in an estimated sensitivity of 1-4 oxygen vacancies imaged with unit cell resolution.¹⁰ The O atomic columns in SrTiO₃ and YBa₂Cu₃O₇ have been imaged directly using aberration-corrected TEM.⁴ Comparison of low-angle strain contrast and high-angle Z-contrast images was used to discriminate between various dopant-point defect complexes responsible for dopant electrical deactivation in Si.¹¹

Aberration correction allows larger numerical apertures which move STEM imaging from the realm of a pure 2D projection into 3D imaging by optical sectioning. Some preliminary results have measured the height of metal catalysts on a a-C support, and suggest that single-atom localization in 3D may be possible.¹² STEM imaging on standard instruments has provided the monotonic response of intensity with thickness necessary for nanometer resolution tomography of crystalline materials.¹³

Finally, coherent scattering at nanometer spatial resolution is emerging as a powerful tool to characterize local structure in amorphous materials. The pair distribution function of volumes as small as 2 nm in diameter can be measured by deconvolution of the convergent probe,¹⁴ which will have applications in determining the structure of thin amorphous reaction layers and intergranular films. Statistical analysis of spatial fluctuations in the diffracted intensity at the nanoscale in the form of fluctuation transmission electron microscopy¹⁵ has revealed structural order in amorphous semiconductors¹⁶ and metallic glass.¹⁷

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